# *Ab-Initio* Cluster Calculations of Hole Transport and Activator Excitation in CsI:Tl and CsI:Na<sup>1</sup>

#### S. E. Derenzo and M. J. Weber

Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720 USA

#### Abstract

We describe methods for using Gausian94 (an ab-initio molecular orbital program) to compute energies and electron distributions that describe (1) the formation and transport of holes in the crystal CsI and (2) the electronic nature of the lowest excited states of CsI, CsI:Tl and CsI:Na. To model these processes, the Schrödinger equation was solved at the Hartree-Fock level (in some cases with Møller-Plesset secondorder electron correlation corrections) for clusters ranging in size from of 12 Cs and 12 I atoms to 16 Cs and 29 I atoms in an electrostatic field generated by approximately 5800 point charges. The calculations show that (1) a relaxed hole in CsI is shared equally by two I atoms (classic V<sub>k</sub> center) bound by an energy of 0.85 eV; (2) the energy barrier for the motion of the hole is 0.15 eV and the transition state consists of the hole on a single I atom; (3) the lowest excited state of Cs<sub>12</sub>I<sub>12</sub> is a V<sub>k</sub> center plus a diffuse electron in the Rydberg states of the other ions (an exciton); (4) the lowest excited state of the cluster NaCs<sub>13</sub>I<sub>14</sub> is an exciton whose energy is lowered by the presence of the Na atom; and (5) the lowest excited state of the cluster TlCs<sub>13</sub>I<sub>14</sub> is an excited Tl atom with all Cs and I electrons in their ground states. We believe that it is now computationally possible to model hole transport and electronic excitation in a variety of compounds to guide the search for new scintillators.

#### I. INTRODUCTION

This work is motivated by the need for better gamma ray detectors for medical imaging, specifically ultra-fast bright scintillators for time-of-flight PET and ultra-bright long-wavelength scintillators for silicon photodiodes. Here we explore the feasibility of making qualitative predictions of the scintillation efficiency of host/activator combinations using *ab-initio* molecular orbital cluster computations. We are particularly interested in processes that differentiate most inorganic crystals from the few that are useful scintillators, such as electron and hole transport in the host, and the sequential capture of electrons and holes to form an excited state at or near an activator atom. For this we do not need high accuracy and do not attempt to predict spectroscopic properties.

Scintillation can be described in three stages [1, 2] with an overall efficiency (photons/MeV) given by

$$= \bullet S \bullet q$$

where is the number of electrons and holes produced per

MeV of ionizing radiation, S is the efficiency with which the electrons and holes transfer their energy to the luminescent center, and q is the quantum efficiency of the excited state of the luminescent center. We are interested in computing the transfer process in two separate, sequential steps:  $S_d$ —the diffusion of electrons and holes in the host crystal, and  $S_e$ —the production of an excited state by the sequential capture of an electron and a hole by an activator atom.

We begin with a test material CsI [3-8], a scintillator of interest in both its pure and activated forms. In CsI:Na and CsI:Tl it is known that  $S_d$  and  $S_e$  are slow (  $\phantom{I}$  10 ns) but efficient processes and that a hole in the host CsI crystal creates a  $V_k$  center—a bound  $\rm I_2^-$  molecule—aligned along the [100] axis.

## II. COMPUTATIONAL METHODS

# A. Program

The Gaussian94 program [9] at the Hartree-Fock (HF) and Møller-Plesset second-order perturbation theory (MP2) levels was used to determine energies and electron population distributions for clusters of atoms in a lattice of point charges. It was quickly found that the standard HF linear solution method was unable to converge for CsI clusters larger than about 15 atoms and hence the slower quadratic convergence method was used for all the results presented here. Atomic relaxation was performed using the numerical Fletcher-Powell method because the more efficient analytic methods are disabled when using point charges. Atomic charges and electron populations were determined from the Natural Population Analysis (NPA) phase of the Natural Bond Orbital (NBO) Analysis [10].

The Gaussian94 runs were performed on Silicon Graphics, Inc. computers with a total of four R10000 processors, and on a Cray J-90 at the National Energy Research Supercomputer Center at LBNL.

#### B. Effective Core Potentials and Basis Functions

The LanL2DZ basis set (provided by the Los Alamos National Laboratory as a standard feature of Gaussian94) was used for the relativistic effective core potentials of the Cs, I, and Tl atoms and for the basis functions of Na and Tl atoms. Because the Los Alamos basis functions for Cs are quite numerous and out of proportion to the simpler I basis functions, we used the simpler form for both Cs and I atoms, and reoptimized the coefficients and exponents by minimizing the ground-state energy of the cluster Cs<sub>2</sub>I<sub>2</sub> in 508 point charges. For the hole formation and transport calculations, diffuse s and d basis functions (with exponents of 0.02 Bohr<sup>-2</sup>) were added to the central row of four or five I atoms. For the excited state

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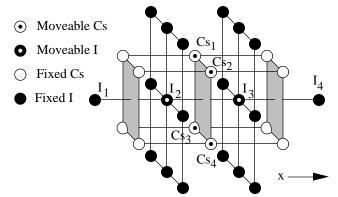
calculations, diffuse s and d basis functions (with exponents of  $0.02 \text{ Bohr}^{-2}$ ) were added to all Cs and I atoms.

# C. Crystal Field Potential

To use Gaussian94 for crystal calculations, it is necessary to provide a finite set of point charges that accurately reproduce the electrostatic potential of the infinite crystal lattice. For the CsI crystal, we use an array of radially balanced Cs4I4 unit cells. This unit cell has zero dipole moments  $q_ix_i,\ q_iy_i,\ q_iz_i$  and is radially balanced in the sense that if the distance from any point to the ith unit cell point charge is  $r_i,$  then  $q_ir_i{}^2=0.$  Even a small array of these unit cells gives excellent agreement between the potential computed using a finite sum over the array of unit cells and the Ewald sum method [11] for the infinite crystal. A 9 x 9 x 9 array of Cs4I4 unit cells was used which yielded errors in the potential of the order of  $10\,\text{mV}$  rms. Additional adjustment of outer atoms to nearby vacant sites was used to further reduce the error to a few mV rms.

# III. HOLE FORMATION IN THE CLUSTER $Cs_{12}I_{20}$

To model hole formation in CsI, we used the cluster  $Cs_{12}I_{20}$  (see Fig. 1) in which two I atoms were surrounded by a sufficient number of atoms to create a realistic environment for motion in the x direction. In addition the four nearest Cs neighbors are allowed to move radially in the coulomb field of the hole. The coordinates of the six moveable atoms are:  $I_2(-a,0,0)$ ,  $I_3(a,0,0)$ ,  $Cs_1(0,b,b)$ ,  $Cs_2(0,-b,b)$ ,  $Cs_3(0,b,-b)$ ,  $Cs_4(0,-b,-b)$ .



**Figure 1.**  $Cs_{12}I_{20}$  cluster used to model hole formation in the CsI host crystal.

#### A. Ground State

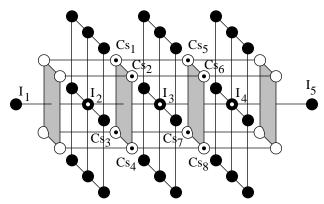
Optimizing the variables a and b from their starting values of 2.284 Å reduced the ground state (neutral singlet) HF energy by only 0.4 mV. The variables also changed by only very small amounts: a = 0.02 Å, b = -0.02 Å. The electron population analysis (EPA) placed all electrons in the expected valence levels; all Cs charges were +1.00 and all I charges were -1.00.

#### B. Hole State

The HF calculation was repeated with a cluster charge one higher than the ground state (+1 doublet). The initial energy was 8.67 eV above the ground state. Optimizing a and b reduced the energy by 0.77 eV to 7.79 eV. The parameters for the relaxed configuration were a = 1.73 Å, b = 2.47 Å. Thus the central  $I_2$  and  $I_3$  moved together from an initial interatomic distance of 4.568 Å to 3.46 Å, and the four nearest-neighbor Cs atoms moved radially outward by 0.19 Å. The EPA showed that the  $I_2$  and  $I_3$  charges were both –0.54. The relaxed hole is therefore a bound  $I_2^-$  molecule, the expected  $V_k$  center.

# IV. HOLE FORMATION AND TRANSPORT IN THE CLUSTER CS<sub>16</sub>I<sub>29</sub>

To provide a large enough cluster to produce a  $V_k$  center on two symmetric sites, we used the cluster  $CS_{16}I_{29}$  with 11 moveable atoms (see Fig.2) in which three I atoms were surrounded by a sufficient number of atoms to permit realistic motion in the x direction and in which the eight nearest Cs neighbors were allowed to move both along the x direction and radially in the coulomb field of the hole.



**Figure 2.**  $Cs_{16}I_{29}$  cluster used to model hole formation and transport in the CsI host crystal. Atom symbols are the same as in Figure 1.

#### A. Ground State

The electron population analysis (EPA) of the ground state HF solution with all atoms at their normal lattice positions placed all electrons in the expected valence levels; all Cs charges were +1.00 and all I charges were -1.00.

#### B. Hole State

Starting with the initial atomic configuration, a HF calculation was performed with a cluster charge one higher than the ground state (+1 doublet). The EPA revealed that the hole was mainly on I<sub>3</sub>, at the center of the cluster:  $q_{I2}=-0.92$ ,  $q_{I3}=-0.16$ ,  $q_{I4}=-0.94$ . A similar result has been reported for NaCl [12]. The energy was 8.36 eV above that of the ground state, similar to that of the  $Cs_{12}I_{20}$  cluster.

Optimizing the seven coordinate variables reduced the energy by 0.85 eV to 7.51 eV. and resulted in the central  $I_3$  and  $I_4$  pulling together symmetrically from an interatomic separation of 4.568 Å to 3.5 Å while the four nearest-neighbor Cs atoms moved radially outward by 0.19 Å. The EPA found that the hole was shared by  $I_3$  and  $I_4$ :  $q_{I2} = -1.00$ ,  $q_{I3} = -0.38$ ,  $q_{I4} = -0.65$ . The outer valence population of  $I_3$  is 5s(1.99), 5p(5.37), 5d(0.01), 6p(0.01) and the outer valence population of  $I_4$  is 5s(1.99), 5p(5.64), 5d(0.01), 6p(0.01). (The inequality of  $I_3$  and  $I_4$  is a manifestation of the asymmetry in the cluster used.) The relaxed hole is again a bound  $I_2$  molecule ( $V_k$  center).

# C. Hole Transport

Because a  $V_k$  center can be formed by either  $I_2$ - $I_3$  or  $I_3$ - $I_4$ , depending on the x coordinate of  $I_3$ , we explored how a  $V_k$  center can be shifted between the two sites by varying the x coordinate of  $I_3$  from 0.0 to 1.2 Å in discrete steps of 0.2 Å. At each value of the x coordinate of  $I_3$ , a ten-atom relaxation of the six parameters was performed. The x coordinates of  $I_2$ ,  $I_3$ ,  $I_4$  and  $x_{hole}$  (the center of charge of the hole) are plotted in Fig. 3 as a function of the x coordinate of  $I_3$ . Values for negative  $I_3$  x coordinates were derived from the positive values by symmetry. Each six-parameter optimization required approximately 300 hours of R10000 processor time.

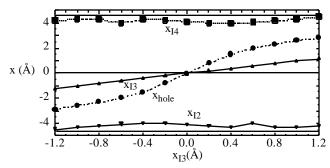
In our previous work where only  $I_2$  and  $I_4$  were allowed to relax at each  $I_3$  position, the HF energy vs.  $x_3$  was almost perfectly flat. Figure 4 shows that some relaxation of the nearby Cs atoms is required to produce a stable  $V_k$  center at the HF level. Adding the effects of electron correlation using MP2, the binding of the  $V_k$  center increases. The importance of MP2 has also been shown for hole formation in NaCl [12]. The results in Fig. 4 also show that the transition state for hole transport in CsI is an unstable one-center configuration that lies 0.15 eV above the relaxed  $V_k$  center configuration.

#### V. GROUND AND EXCITED STATES OF CS<sub>12</sub>I<sub>12</sub>

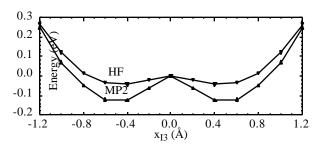
# A. Choice of Model and Ground State

The excited state can take the form of an electron promoted to a higher orbital in the same atom, to an orbital in a different atom, or to a delocalized orbital that occupies a volume of space containing many atoms. In the last case, it is necessary to use diffuse basis functions. When we attempted the excited state (triplet) calculation of  $Cs_{12}I_{12}$  (Fig. 5) without diffuse basis functions, the resulting energy is much too high, 15 eV above the ground state, far above the known exciton energy of 5.3 eV known from band structure calculations [13] and photoemission studies [14, 15]. This high energy is the result of the inability of the basis set to describe the extended nature of the excited electron.

As shown below, when the calculation is repeated with diffuse s and d basis functions added to all atoms, and the central two I atoms are placed at the  $V_k$  separation found before, the energy is much lower, 5.9 eV above the ground state and in much better agreement with the expected energy.



**Figure 3.** X coordinates of  $I_2$ ,  $I_4$ , and  $x_{hole}$  (the center of charge of the hole) as the x coordinate of  $I_3$  is varied.



**Figure 4.** Energy at the HF and MP2 levels of theory as the x coordinate of  $I_3$  is varied. The two stable configurations at  $x_{I3} = -0.5$  Å and +0.5 Å are  $V_k$  centers at the  $I_2$ - $I_3$  and  $I_3$ - $I_4$  sites, respectively.

However, the addition of these diffuse s and d basis functions increases the computation time by approximately a factor of 10, which compelled us to reduce the size of the cluster to  $Cs_{12}I_{12}$ , the minimum size that cages the central two I atoms with their eight nearest Cs neighbors and their six nearest I neighbors (see Fig. 5). It is important to add the diffuse basis functions to all the atoms of the cluster, because when they are added to a selected set of atoms, the excited electron will be artificially localized to those atoms.

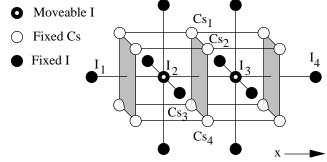


Figure 5: Cluster used to model excitation of the CsI crystal.

The electron population analysis (EPA) of the ground state HF solution with all atoms at their normal lattice positions placed all electrons in the expected valence populations; all Cs charges were +1.00 and all I charges were -1.00.

## B. Excited State

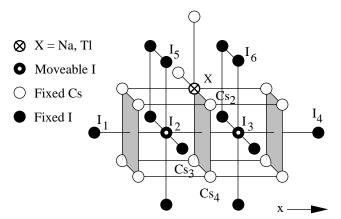
The excited state of the system with  $I_2$  at (-a, 0, 0) and  $I_3$  at (a, 0, 0), a = 1.73 Å  $(V_k$  center) has an energy 5.87 eV above the ground state. The EPA analysis showed that the

central two I atoms ( $I_2$ – $I_3$ ) had charges of –0.45 and outer valence populations 5s(1.96), 5p(5.49), 5d(0.01), the nearest four Cs atoms ( $Cs_1$ – $Cs_4$ ) had charges +0.85 and outer valence populations 6s(0.13), 5d(0.02), and the remaining negative charge was distributed in the 5d and 6s orbitals of the other 18 atoms. The valence population of the excited electron is virtually identical to that of an excess electron in the ground state cluster. This calculation describes the excited state of CsI as a hole ( $V_k$  center) plus an electron in the higher orbitals of the nearby atoms, which is the expected electronic configuration of an exciton.

# VI. GROUND AND EXCITED STATES OF NACS<sub>13</sub>I<sub>14</sub>

# A. Choice of Model and Ground State

To describe the excited state of CsI:Na, one Cs atom was replaced with a Na atom and four additional atoms were added to surround the Na atom with its nearest 14 atoms (see Fig. 6). The Los Alamos basis set for Na includes diffuse s and p orbitals with exponents quite close to 0.02 Bohr<sup>-2</sup>.



**Figure 6:** Cluster used to model hole and electron capture by Tl and Na atoms to form the excited state.

The ground state EPA shows that the Na charge is +0.77 and the outer valence population is 3s(0.22). The eight nearest neighbor I atoms have charge -0.98 and outer valence populations 5s(1.98), 5p(5.99). All other Cs and I atoms have their expected valence populations.

## B. Excited State

The excited state of the system with  $I_2$  at (-a, 0, 0) and  $I_3$  at (a, 0, 0), a = 1.73 Å  $(V_k$  center) has an energy 5.24 eV above the ground state. The central I atoms  $(I_2-I_3)$  have charges -0.45 and outer valence populations 5s(1.95), 5p(5.48), 5d(0.01), 6s(0.01). The Na atom has a charge of +0.76 and outer valence population 3s(0.21), 3p(0.01), 4s(0.01), essentially identical to the ground state. The Cs atom nearest to the NaI2 subcluster  $(Cs_2)$  has a charge +0.67 and outer valence population 5d(0.15), 6s(0.20). The next nearest Cs atoms  $(Cs_3, Cs_4)$  have charge +0.90 and outer valence populations 6s(0.10), 5d(0.01). The two I atoms nearest the NaI2 subcluster  $(I_5, I_6)$  have charges -1.13 and outer valence populations 5s(1.97), 5p(5.96), 5d(0.18), 6s(0.02). The

valence population of the excited electron is similar to that of an excess electron in the ground state cluster. This calculation describes the excited state of CsI:Na as a hole ( $V_k$  center) plus an electron in the higher orbitals of the nearby atoms, similar to the CsI exciton. The Na atom is not directly involved in the excitation. However, the Na atom appears to energetically bind the exciton because the excited state minus ground state energy of the CsI:Na cluster is 0.63 eV below the excited state minus ground state energy of the CsI cluster.

# VII. GROUND AND EXCITED STATES OF TLCs<sub>13</sub>I<sub>14</sub>

# A. Choice of Model and Ground State

The ground state EPA shows that the Tl charge is +0.33 and the outer valence population is 6s(2.00), 6p(0.66), 7p(0.01). The eight nearest neighbor I atoms have charge -0.93 and outer valence populations 5s(1.97), 5p(5.96). All other Cs and I atoms have their expected valence populations.

## B. Excited State

The excited state of the system with atoms in their normal lattice positions has an energy 5.02 eV above the ground state. The EPA shows that the Tl charge is +0.18 and the outer valence population is 6s(1.21), 6p(1.34), 7p(0.28). The eight nearest neighbor I atoms have charge -0.90 and outer valence populations 5s(1.97), 5p(5.93). All other Cs and I atoms have their expected valence populations. Note that unlike the CsI and CsI:Na clusters, there is no localized hole. Essentially the only difference between the excited state and the ground state is that the 6p and 7p Tl orbitals have gained 0.95 electron and the 6s has lost 0.79 electron. The calculation shows that the excited state of CsI:Tl involves promoting an electron within the Tl orbitals. The Cs and I atoms are only slightly affected.

### VIII. SUMMARY

By *ab-initio* molecular orbital calculation of the energies and electron populations of clusters of atoms imbedded in point charges, we have been able to show the following:

- A missing electron (hole) in CsI is a pair of I atoms (a classic V<sub>k</sub> center) bound by an energy of 0.85 eV.
- The energy barrier for hole transport in the [100] direction is 0.15 eV. The transition state for V<sub>k</sub> diffusion is a hole on a single I atom.
- The lowest excited state of Cs<sub>12</sub>I<sub>12</sub> is a V<sub>k</sub> center plus a diffuse electron in the Rydberg states of the other ions (an exciton).
- The lowest excited state of the cluster NaCs<sub>13</sub>I<sub>14</sub> is an exciton whose energy is lowered by the presence of the Na atom
- The lowest excited state of the cluster TlCs<sub>13</sub>I<sub>14</sub> has an excited Tl atom and all Cs and I electrons are in their ground states.

#### IX. CONCLUDING COMMENTS

This work was intended as a feasibility study of what could be done with currently available software and hardware. Clearly it would be desirable to continue this work using larger clusters of atoms in more complete states of relaxation, a larger number of basis functions, and at the highest feasible level of theory. However these aspirations are severely limited by the computation time, which increases as the 4th power of the number of atoms. However, considerable factors in computation speed would be possible with the following software improvements:

- Algorithms designed for more reliable convergence of the Hartree-Folk equations, especially for systems with diffuse electrons. Even the slow quadratic convergence method can fail in such cases.
- Atom position relaxation, using analytical gradients and second derivatives. (Currently when using point charges only numerical optimization is available.) This could increase the computation speed by a factor of 10.
- Replacement of ground-state boundary atoms with pseudopotentials [16]. This reduces greatly the number of electrons that are explicitly treated while preserving natural motion of the inner atoms during relaxation, and could increase the computation speed a factor of 10 to 100

Additional useful features would include

- Excited state calculations at the MP2 level
- Inclusion of spin-orbit coupling, which is necessary to compute (1) more accurate energy levels for heavy atoms and (2) the amount of triplet-singlet mixing and the radiative emission rate.
- Determination of the lowest triplet energy where the triplet and ground-state configuration potential energy surfaces cross. This is necessary for determining the thermal quenching temperature.

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